

# The Crystal Structure of Pentathiazyl Tetrachloroaluminate, $S_5N_5AlCl_4$

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X-Ray diffraction shows pentathiazyl tetrachloroaluminate to be orthorhombic,  $a=9.412$  Å,  $b=13.647$  Å,  $c=20.761$  Å, space group  $Pnma$ ; there are 8 formula units per cell.

Least squares refinement with 1523 reflections gave a final  $R$ -value of 0.087 for 145 parameters. The intensity data were collected on a semi-automatic diffractometer using monochromatized  $MoK\alpha$ -radiation.

The compound consists of discrete  $S_5N_5^+$  and  $AlCl_4^-$  ions. The  $S_5N_5^+$  cation is heart shaped and almost planar; it deviates significantly from symmetries  $mm2$ , and  $2$ . The S-N distances range from 1.465 Å to 1.590 Å with a mean e.s.d. of 0.009 Å, the mean value is 1.539 Å, e.s.d. 0.003 Å. The mean Al-Cl distance is 2.117 Å, e.s.d. 0.007 Å.

**P**entathiazyl tetrachloroaluminate,  $S_5N_5AlCl_4$ , the first stable salt of the  $S_5N_5^+$  cation, has been prepared<sup>1</sup> by Banister and Dainty, and a preliminary report<sup>1</sup> of the crystal structure has been given. This article describes the crystal structure determination in more detail and its refinement using more data than were originally available.

## EXPERIMENTAL

The crystals which had been crystallised from thionyl chloride were kindly provided by Drs. J. A. Banister and P. J. Dainty.

Intensity data were collected using a linear diffractometer of the Arndt-Phillips<sup>2</sup> design.  $MoK\alpha$ -radiation monochromatized<sup>3</sup> by means of a graphite crystal was employed in conjunction with a scintillation counter and a pulse height analyser. The background-peak-background technique was used. As the crystals are very moisture sensitive, the crystal used was sealed in a capillary tube. It was mounted with its [010] axis, the needle axis, as rotation axis.

A total of 3229 reflections for which  $I > 2\sigma_c(I)$  where  $\sigma_c(I)$  is the square-root of the total number of counts per reflection were measured. These were the data used for the preliminary structure determination.<sup>1</sup> The data were later remeasured using a slower scan giving a total of 1523 reflections having  $I > 2\sigma_c(I)$ .

The crystal used was 1.2 mm in length and 0.18 by 0.16 mm in cross section. No correction was made for absorption.



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Table 1. Continued.

Table with multiple columns of numerical data. Each row contains a sequence of numbers, some with leading zeros, representing a dataset. The numbers range from approximately -400 to 400. The table is organized into columns, with some rows starting with a small number (1-3) followed by a larger number (10-19) and then the data values.

## CRYSTAL DATA

$S_5N_5AlCl_4$ ,  $M=399.1$ . Orthorhombic,  $a=9.412 \text{ \AA}$ ,  $b=13.647 \text{ \AA}$ ,  $c=20.761 \text{ \AA}$ ,  $U=2667 \text{ \AA}^3$ ,  $Z=8$ ,  $D_c=1.99$ ,  $F(000)=1568$ . The possible space groups are  $Pnma$  ( $D_{2h}^{16}$ , No. 62) and  $Pn2_1a$  ( $C_{2v}^9$ , No. 33); intensity statistics and morphology show the space group to be  $Pnma$ . The crystals form pale yellow prisms bounded by  $\{102\}$  and terminated by  $\{011\}$ . This morphology violates the Donnay-Harker law.<sup>4</sup>

Table 2. Atomic coordinates as fractions of cell edges. The estimated standard deviations  $\times 10^4$  are given in brackets.

	$x$	$y$	$z$
Al 1	0.4662 (4)	-0.2500 (0)	0.3801 (2)
Al 2	-0.0554 (4)	0.2500 (0)	0.3693 (2)
Cl 1	0.5914 (3)	-0.1222 (2)	0.3675 (1)
Cl 2	0.2998 (4)	-0.2500 (0)	0.3114 (2)
Cl 3	0.3771 (4)	-0.2500 (0)	0.4743 (2)
Cl 4	-0.1763 (3)	0.1212 (2)	0.3869 (1)
Cl 5	0.1231 (4)	0.2500 (0)	0.4319 (2)
Cl 6	0.0151 (6)	0.2500 (0)	0.2723 (2)
S 1	-0.0212 (3)	-0.1040 (3)	0.3191 (2)
S 2	0.2074 (4)	0.0297 (3)	0.2700 (1)
S 3	0.4191 (3)	0.1096 (2)	0.3678 (2)
S 4	0.3009 (3)	0.0122 (2)	0.4811 (1)
S 5	0.0650 (3)	-0.1062 (2)	0.4528 (1)
N 1	0.0877 (10)	-0.0366 (8)	0.2951 (4)
N 2	0.3121 (9)	0.0670 (7)	0.3161 (5)
N 3	0.4006 (7)	0.0782 (6)	0.4410 (4)
N 4	0.1856 (7)	-0.0321 (5)	0.4361 (4)
N 5	-0.0224 (8)	-0.1296 (6)	0.3923 (4)

Table 3. Thermal vibration parameters (in  $\text{\AA}^2 \times 10^{-4}$ ) and, in brackets, their estimated standard deviations.

	$u_{11}$	$u_{22}$	$u_{33}$	$u_{12}$	$u_{13}$	$u_{23}$
Al 1	376 (23)	411 (19)	632 (27)	0 (0)	13 (20)	0 (0)
Al 2	593 (27)	426 (19)	429 (23)	0 (0)	69 (20)	0 (0)
Cl 1	810 (19)	666 (16)	1028 (22)	-309 (17)	133 (17)	41 (17)
Cl 2	596 (26)	984 (29)	804 (29)	0 (0)	-159 (22)	0 (0)
Cl 3	680 (25)	629 (21)	623 (24)	0 (0)	127 (20)	0 (0)
Cl 4	798 (18)	596 (14)	677 (16)	-254 (15)	30 (14)	-30 (14)
Cl 5	397 (21)	736 (24)	913 (30)	0 (0)	17 (20)	0 (0)
Cl 6	1533 (44)	870 (29)	521 (25)	0 (0)	408 (27)	0 (0)
S 1	984 (24)	1004 (23)	1052 (25)	294 (22)	-521 (21)	-398 (22)
S 2	1353 (29)	1273 (28)	532 (17)	628 (26)	199 (19)	236 (21)
S 3	634 (18)	676 (17)	1706 (35)	8 (18)	404 (21)	357 (22)
S 4	658 (18)	762 (18)	702 (18)	-73 (16)	-164 (15)	3 (17)
S 5	612 (16)	702 (17)	757 (18)	-72 (15)	13 (14)	142 (16)
N 1	1133 (77)	1078 (75)	994 (75)	384 (71)	340 (65)	240 (69)
N 2	720 (66)	981 (73)	1682 (100)	291 (64)	31 (68)	-227 (76)
N 3	539 (50)	536 (48)	1205 (72)	-12 (47)	-126 (51)	-72 (52)
N 4	452 (44)	506 (42)	694 (51)	76 (41)	-66 (39)	32 (43)
N 5	724 (56)	708 (56)	1026 (64)	6 (54)	-234 (52)	-39 (56)

Table 4. The results of the constrained refinements compared with that for the unconstrained refinement.

	<i>R</i>	$\sum w\Delta^2$	Number of parameters
(a) $S_5N_5^+$ with symmetry <i>mm</i> 2	0.096	5248	130
(b) $S_5N_5^+$ with symmetry 2	0.093	4817	133
(c) No constraint	0.087	4310	145
$\mathcal{R}(a/b) = 1.044$ $\mathcal{R}(b/c) = 1.057$	(1523 observations)	$\mathcal{R}(0.001) = 1.005$ $\mathcal{R}(0.001) = 1.011$	

Table 5. Bond distances in Å. The estimated standard deviations (in Å × 10<sup>-4</sup>) are shown in brackets.

	<i>l</i>	$\sigma(l)$
S 1-N 1	1.465	(10)
S 2-N 1	1.536	(10)
S 2-N 2	1.465	(10)
S 3-N 2	1.582	(10)
S 3-N 3	1.590	(9)
S 4-N 3	1.545	(8)
S 4-N 4	1.554	(7)
S 5-N 4	1.559	(7)
S 5-N 5	1.535	(9)
S 1-N 5	1.558	(9)
Al 1-Cl 1	2.121	(3)
Al 1-Cl 2	2.119	(6)
Al 1-Cl 3	2.093	(5)
Al 2-Cl 4	2.126	(3)
Al 2-Cl 5	2.124	(5)
Al 2-Cl 6	2.121	(5)

Table 6. Bond angles and their estimated standard deviations in degrees. Primed atoms are related to the corresponding unprimed atom by reflection through the mirror plane.

	$\theta$	$\sigma(\theta)$
N 5-S 1-N 1	118.5	0.5
S 1-N 1-S 2	177.1	0.8
N 1-S 2-N 2	118.4	0.6
S 2-N 2-S 3	177.3	0.7
N 2-S 3-N 3	118.6	0.5
S 3-N 3-S 4	137.7	0.5
N 3-S 4-N 4	109.1	0.4
S 4-N 4-S 5	128.9	0.5
N 4-S 5-N 5	110.1	0.4
S 5-N 5-S 1	138.4	0.6
Cl 1-Al 1-Cl 1'	110.6	0.2
Cl 1-Al 1-Cl 2	109.1	0.2
Cl 1-Al 1-Cl 3	109.6	0.2
Cl 2-Al 1-Cl 3	108.7	0.2
Cl 4-Al 2-Cl 4'	111.6	0.2
Cl 4-Al 2-Cl 5	108.5	0.1
Cl 4-Al 2-Cl 6	109.3	0.2
Cl 5-Al 2-Cl 6	109.5	0.3

Observed and calculated structure factors, atomic coordinates, and thermal vibration parameters, are listed in Tables 1–3. Bond distances and angles are given in Tables 5 and 6.

### STRUCTURE DETERMINATION

An attempt was made to solve the structure by direct methods using Danielsen's <sup>5</sup> program SYMBAD. The resulting E-map could not be interpreted to give the structure, and selected combinations of peaks all led to very high *R*-values. The Patterson function was difficult to interpret but two possible atomic positions (Cl 1 and Cl 4) were recognized as having occurred on the E-map. Systematic examinations of the 20 highest peaks from the E-map showed that there were four peaks which gave interatomic vectors all consistent with the Patterson function. A Fourier synthesis based on signs calculated from these four atoms contained many peaks several of which were false. Since the constitution of the compound was not known, several cycles of structure factor-Fourier calculations were needed before the structure could be established.

The first four atoms found were: S 2, Cl 1, Cl 2, and Cl 4. Examination of the E-map later showed that for only one more of the heavier atoms was there a corresponding peak on the E-map whereas for the other atoms there was usually a peak at a position related to the correct one by some false symmetry, *e.g.* *x, y, -z*.

We have found <sup>6</sup> the combined use of Patterson and direct methods an efficient way of dealing with structures that for various reasons are not easily solved by either method alone.

### REFINEMENT

Least-squares refinement of atomic coordinates, thermal parameters, and scale factor was carried out using the block diagonal technique. The final *R*-value obtained was 0.087 for 145 parameters, the weighted *R*-value was 0.072.

In order to test the significance of the deviations of the  $S_5N_5^+$  ion from symmetries *mm*2, and 2, constrained refinements were carried out. The results are given in Table 4 and show that the molecule deviates significantly from these symmetries.

### COMPUTATIONAL DETAILS

The block-diagonal least-squares refinement was carried out using an ALGOL program (G 403), the quantity minimised was

$$r = \frac{\sum w ||F_o| - |F_c||^2}{\sum w |F_o|^2}$$

where  $w = 1/\sigma^2$  and  $\sigma = \sqrt{\sigma_c(F^2) + (1+K)F^2 - |F|}$ , *K* was varied so that  $\langle w ||F_{obs}| - |F_{calc}||^2 \rangle$  varied as little as possible with the magnitude of  $F_{obs}$ . The final value of *K* was 0.025.

The constrained refinements were carried out using Pawley's modification <sup>7</sup> of the ORFLS program. The weights used for these refinements were the same as those from the final unconstrained refinement.

The atomic scattering factors used for the block-diagonal refinement were those of International Tables <sup>8</sup> approximated by Bassi <sup>9</sup> polynomials, and for the constrained refinement those of Cromer and Mann.<sup>10</sup>

## DISCUSSION

The structure consists of discrete  $S_5N_5^+$  and  $AlCl_4^-$  ions, the  $S_5N_5^+$  ion is in a general position whilst the  $AlCl_4^-$  ions are on two special positions, on mirror planes, as is shown in Fig. 1. Bond distances and angles are given in Tables 5 and 6. Bond distances and angles are not corrected for thermal vibration since attempts at rigid body refinement showed that it is physically unreasonable to treat the  $S_5N_5^+$  ion as a rigid body. The only S-Cl or N-Cl distances less than 3.5 Å are Cl 4-S 4 (3.492 Å) and Cl 4-S 5 (3.495 Å).

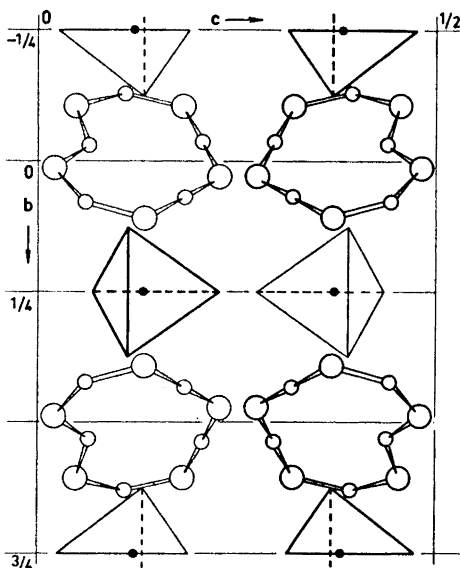


Fig. 1. Part of the structure viewed down the  $a$ -axis. The sulphur atoms are shown as big open circles, the nitrogen atoms as small open circles, the aluminium atoms as full circles, and the chlorine atoms as the vertices of the tetrahedra.

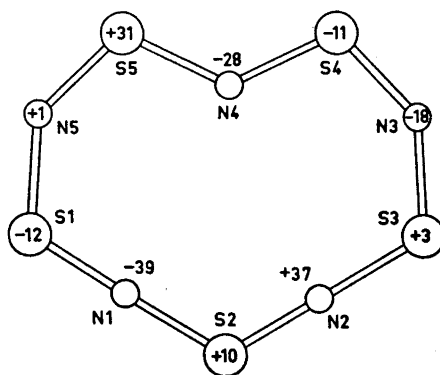


Fig. 2. The  $S_5N_5^+$  cation projected onto the least-squares best plane through the atoms. The deviations of the atoms from the plane, in  $\text{\AA} \times 10^{-3}$ , are also given.

The  $AlCl_4^-$  ions are close to being tetrahedral, the mean Al-Cl distance is 2.117 Å with e.s.d. 0.002 Å which is in accordance with the distance found <sup>11</sup> in  $NaAlCl_4$  (2.13 Å). The distances in  $AlCl_3 \cdot C_6H_5COCl$  are <sup>12</sup> 2.079 Å with

e.s.d. 0.002 Å, and 2.094 Å with e.s.d. 0.003 Å. The two crystallographically independent  $\text{AlCl}_4^-$  ions are arranged symmetrically about the centre of the cation.

The  $\text{S}_5\text{N}_5^+$  ion is heart-shaped and almost planar although not accurately so. The deviations from planarity are shown on Fig. 2 and in Table 7 which

Table 7. Atomic coordinates of the  $\text{S}_5\text{N}_5^+$  ion in Å relative to the inertial axes. The mean standard deviations are 0.003 Å for a sulphur atom coordinate and 0.008 Å for nitrogen.

	<i>x</i>	<i>y</i>	<i>z</i>
S 1	-0.0123	-0.6730	2.5901
S 2	0.0101	-2.3047	0.0723
S 3	0.0027	-0.7977	-2.5753
S 4	-0.0113	1.9033	-1.4567
S 5	0.0313	1.9383	1.3512
N 1	-0.0388	-1.4764	1.3654
N 2	0.0372	-1.5958	-1.2096
N 3	-0.0184	0.7913	-2.5287
N 4	-0.0279	1.2501	-0.0465
N 5	0.0011	0.8794	2.4615

gives the atomic coordinates of the ring in Å relative to the inertial axes of the cation. The ring deviates significantly from planarity, being folded so that there are two nodes approximately parallel to the line joining atoms S 1 to S 4. The deviations from planarity are similar to those found in medium sized aromatic hydrocarbons such as pyrene<sup>13,14</sup> and ovalene;<sup>15</sup> in solution the cation would presumably be planar.

The mean S–N distance is 1.539 Å which indicates a considerable measure of double bonding. The bonds are not all equal and vary from 1.465 Å to 1.590 Å. The differences are considerably in excess of the estimated standard deviations and furthermore the differences do not seem to arise from systematic errors in the data since the  $\text{AlCl}_4^-$  tetrahedra show little deviation from regularity. The angles at the sulphur atoms are quite similar, ranging from 109.1° to 118.5° with a mean values of 115° whereas there is a much bigger spread of the S–N–S angles, 128.9° to 177.3°.

The short S–N bonds are some of the shortest so far observed in sulphur–nitrogen ring systems; comparable values are 1.49 Å in  $\text{S}_4\text{N}_3^+$  (Ref. 16) and 1.54 Å in  $\text{S}_3\text{N}_2\text{Cl}^+$  (Ref. 17).

The nature of the bonding is discussed by Adams *et al.*<sup>18</sup> in the light of their ESCA measurements. Molecular orbital calculations are being carried out on the  $\text{S}_5\text{N}_5^+$  system by Zahradnik.<sup>19</sup>

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